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(54) **FLUOROPOLYMER, PROCESS FOR PREPARING THE SAME, AND USE THEREOF**

(57) A fluorine-containing polymer, having a number-average molecular weight of 500 to 100,000 and represented by the following general formula

$$\text{Rf}-(\text{OC}_3\text{F}_6)_a-(\text{OC}_2\text{F}_4)_b-(\text{OCF}_2)_c-\text{X}-\text{Y}-\text{Z}-\text{MP}-\text{P}_n\text{R}_m$$

or

$$\text{P}_n\text{R}_m-\text{M}-\text{Z}-\text{Y}-\text{X}-(\text{OC}_3\text{F}_6)_a-(\text{OC}_2\text{F}_4)_b-(\text{OCF}_2)_c-\text{X}-\text{Y}-\text{Z}-\text{MP}_n\text{R}_m$$

(wherein Rf is a perfluoroalkyl group; a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1; X is a group represented by the formula: $-(\text{O})_d-(\text{CF}_2)_e-(\text{CH}_2)_f$; Y is a divalent polar group; Z is a group represented by the formula: $-(\text{CH}_2)_g$; M is a metal atom; R is a hydrocarbon group; P is a hydrolyzable polar group; m is an integer equal to "(valency of M) - 1"; and n is an integer of 1 to m), exhibits excellent stainproof property against oily dirt and can form on a substrate a stainproof layer having an excellent stainproof property against particularly fingerprints.

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Description

FIELD OF THE INVENTION

- 5 [0001] The present invention relates to a fluorine-containing polymer, a process for preparing the polymer, and the use of the polymer, for example, in a stainproof substrate having a stainproof layer of said polymer on a surface thereof.

RELATED ART

- 10 [0002] Materials such as metals, glass and resins are used as general-purpose substrates for a variety of articles such as automotive parts, OA apparatus and home electric appliances. The surfaces of these substrates are liable to get stained by the adhesion of dust particles suspended in the atmosphere of car interior, office interior, room interior and the like, and by the adhesion of oily substances which are contained in foods, oils for machines and the like and are difficult to be wiped off, and also by the adhesion of fingerprints of users. Therefore, these substrates need to be sub-
15 jected to a stainproof treatment so that the substrate surface is rendered less adherent to dirt and the dirt once adhered can be easily removed.

- [0003] As to the stainproof treatment of glass surface, publications such as Japanese Patent Application Laid-Open No. 126244/1989 (JP-A-1-126244) disclose techniques wherein coating films are formed either by direct application of a polymeric substance such as a polydimethylsiloxane to the glass surface or by immersion of glass in a treatment
20 agent containing such a polymeric substance. Also known is a technique wherein a chemical absorption fluorine-containing monomolecular film is formed on the glass surface (see JP-A-4-132637, etc.).

- [0004] As to the stainproof treatment of metal surface, Japanese Patent Kokoku Publication No. 53913/1995 (JP-B-7-53913) discloses a technique relating to an organic composite-plated steel plate by the steps of forming a chromate coating containing a silica sol silane coupling agent on a galvanized steel and thereafter forming a thin layer with an
25 isocyanate-based paint composition.

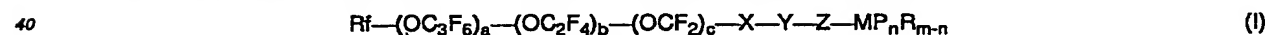
[0005] However, the above-described treatments of prior arts do not provide a sufficient stainproof against oily dirt. In addition, the prior art treatments are associated with the problem that fingerprints tend to adhere to the substrate surface which is touched with fingers and the removal therefrom of the fingerprints is difficult.

30 SUMMARY OF THE INVENTION

[0006] A first object of the present invention is to provide a fluorine-containing polymer which can form on a substrate a stainproof layer exhibiting an excellent stainproof property against oily dirt, particularly fingerprints, as well as a process for preparing the polymer.

- 35 [0007] A second object of the present invention is to provide a stainproof substrate which exhibits an excellent stainproof property against oily dirt, particularly against fingerprints, as well as a process for preparing the substrate.

[0008] According to the present invention, the first object can be achieved by a fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (I):



wherein Rf is a perfluoroalkyl group;

- 45 a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1;

X is a group represented by the formula: $-(O)_d-(CF_2)_e-(CH_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula);

Y is a divalent polar group;

- 50 Z is a group represented by the formula: $-(CH_2)_g-$ (where g is 0 or a number equal to or greater than 1);

M is a metal atom;

R is a hydrocarbon group;

P is a hydrolyzable polar group;

m is an integer equal to "(valency of M) - 1";

- 55 n is an integer of 1 to m;

with the proviso that the presence order of the bracketed repeating units is arbitrary in the formula; $-OC_3F_6-$ represents either $-OCF_2CF_2CF_2-$ or $-OCF(CF_3)CF_2-$; and $-OC_2F_4-$ represents either $-OCF_2CF_2-$ or $-OCF(CF_3)-$.

[0009] A preferred example of the fluorine-containing polymer (I) is a fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (III):



wherein Rf, X, Y, Z, P and R are the same as defined above, and n is an integer of 1 to 3, with the proviso that a is a number equal to or greater than 1.

[0010] Likewise, the first object can be achieved by a fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (II):



wherein X, Y, Z, M, P, R, a, b, c, m and n are the same as defined above.

[0011] In the general formulae (I) and (III), Rf may be any perfluoroalkyl group contained in known fluorine-containing organic polymers, and may be, for example, a linear or branched perfluoroalkyl group having 1 to 16 carbon atoms. Preferably, Rf is CF_3- , C_2F_5- or C_3F_7- .

[0012] In the general formulae (I) and (II), a, b and c represent, respectively, the numbers of the three-type repeating units in the perfluoropolyethers constituting the main skeleton of the fluorine-containing polymer, wherein a, b and c are each 0 or a positive number equal to or greater than 1, with the proviso that $a+b+c$ is at least 1. Preferably, a, b and c are independently selected from 0 and a number in the range of from 1 to 200. More preferably, a, b and c are each 1 to 100 when the number-average molecular weight of the fluorine-containing polymer is taken into consideration.

[0013] The presence orders of the repeating units in brackets having subscripts a, b and c are described according to specific presence orders in the general formulae (I) and (II) for the purpose of convenience. However, the linkage orders of these repeating units are arbitrary without being limited by these orders.

[0014] In the general formulae (I), (II) and (III), X is a group represented by the formula: $-(\text{O})_d-(\text{CF}_2)_e-(\text{CH}_2)_f-$. In this formula, d, e and f independently represent 0 or a positive number equal to or greater than 1 (e.g., 1 to 50), with the proviso that $e+f$ is at least 1, and the presence order of the repeating units in brackets having subscripts d, e and f is not limited in the formula. Preferably, d, e and f are each 0, 1 or 2. More preferably, d is 0 or 1, e is 2, and f is 0 or 1.

[0015] In the general formulae (I), (II) and (III), Y is a divalent polar group. Examples of the divalent polar group may include $-\text{COO}-$, $-\text{OCO}-$, $-\text{CONH}-$, $-\text{NHCO}-$, $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$, $-\text{COS}-$, $-\text{SCO}-$ and $-\text{O}-$. Preferably, Y is $-\text{COO}-$, $-\text{CONH}-$, $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$ or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}-$.

[0016] In the general formulae (I), (II) and (III), Z is a group represented by the formula: $-(\text{CH}_2)_g-$. In this formula, g represents 0 or a positive number equal to or greater than 1 (e.g., 1 to 50). Preferably, g is 0, 1, 2 or 3.

[0017] In the general formulae (I), (II) and (III), M is a metal atom. Examples of the metal atom may include metallic elements which constitute Groups 1 to 15 (e.g., Si, Al and Ti) of the Periodic Table.

[0018] In the general formulae (I) and (II), m is equal to "(valency of M) - 1", and 0 or a positive number, while n is an integer of 1 to m. The valency of M is ordinarily 1 to 5, for example, 2 to 5, and particularly 3 to 5.

[0019] In the general formula (III), n is an integer of 1 to 3.

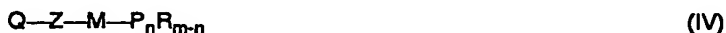
[0020] For example, in the case where M is silicon (Si), m is 3, and n is 1, 2 or 3. Meanwhile, in some cases, the fluorine-containing polymer is present as a mixture of polymers which are represented by the general formula (I), (II) or (III) and have different values for n. If the fluorine-containing polymer is present as a mixture of polymers as described above, n can be given as an average in the mixture.

[0021] In the general formulae (I), (II) and (III), the hydrocarbon group represented by R is preferably a hydrocarbon group containing 1 to 5 carbon atoms. Specific examples of the hydrocarbon group may include alkyl groups such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ and $-\text{C}_3\text{H}_7$.

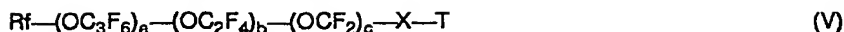
[0022] Examples of the hydrolyzable polar group represented by P may include halogen, $-\text{OA}$, $-\text{OCoA}$, $-\text{O}-\text{N}=\text{C}(\text{A})_2$ (where A is an alkyl group such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ and $-\text{C}_3\text{H}_7$).

[0023] The number-average molecular weight of the fluorine-containing polymer is ordinarily 500 to 100,000. If the number-average molecular weight is less than 500, the polymer is useless because good properties of a polymer are not exhibited. On the other hand, if the number-average molecular weight is more than 100,000, the processability of the polymer is impaired. Preferably, the number-average molecular weight is 1,000 to 10,000.

[0024] The polymer (I) can be prepared by the reaction preferably between a compound represented by the following general formula (IV):



wherein Z, M, P, R, m and n are the same as defined above, and Q is a polar group, and either a compound represented by the following general formula (V):



wherein Rf, X, a, b and c are the same as defined above, and T is a polar group, or a compound represented by the following general formula (VIII):

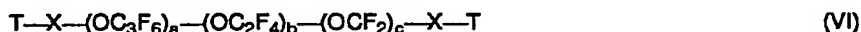


wherein Rf, X and a are the same as defined above, and T is a polar group.

[0025] Further, the polymer (II) can be synthesized by the reaction preferably between a compound represented by the following general formula (IV):



wherein Z, M, P, R, m and n are the same as defined above, and Q is a polar group, and a compound represented by the following general formula (VI):

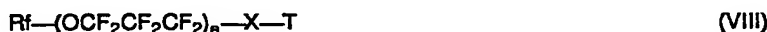


wherein X, a, b and c are the same as defined above, and T is a polar group.

[0026] Furthermore, the polymer (III) can be prepared by the reaction preferably between a compound represented by the following general formula (VII):

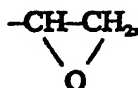


wherein Z, P and R are the same as defined above, n is an integer of 1 to 3, and Q is a polar group, and a compound represented by the following general formula (VIII):



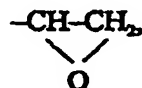
wherein Rf, X and a are the same as defined above, and T is a polar group.

[0027] Examples of the polar group represented by Q may include —OH, —NH₂, —SH,



—Hal (halogen) and —COOH.

[0028] Examples of the polar group represented by T may include —OH, —COOH, —NH₂,



and —CO—Hal (acid halide).

[0029] The second object of the present invention can be achieved by a stainproof substrate comprising a substrate, and a layer of the fluorine-containing polymer presented by the general formula (I), (II) or (III) on the substrate.

[0030] The polymer layer can be formed by applying a separately prepared polymer (I), (II) or (III) to the substrate surface. On the other hand, in a preferred embodiment the polymer layer (I), (II) or (III) can be formed by a process comprising forming on the substrate surface a layer of a compound represented by the general formula (IV) and reacting therewith a compound represented by the general formula (V) or (VI) or alternatively by a process comprising forming on the substrate surface a layer of a compound presented by the general formula (VII) and reacting therewith a compound represented by the general formula (VIII).

[0031] In the case where a layer of the fluorine-containing polymer is formed by a coating method, a solution, suspension liquid or dispersion liquid of the fluorine-containing polymer is coated on the substrate surface, and then is dried.

The coating method may be a conventionally known one and examples of the coating method may include spraying, spin coating, immersion, roll coating, gravure coating and curtain flow coating.

[0032] A solvent in which the polymer is dissolved, suspended or dispersed is not particularly limited. Preferred examples of the solvent may include perfluorohexane, perfluoro-1,3-dimethylcyclohexane and dichloropentafluoropropane (HCFC-225).

[0033] In the case where a layer of the fluorine-containing polymer is formed by successively applying a compound (IV) and a compound (V) to the substrate surface and reacting the two compounds, and examples of the method for coating the compounds (IV) and (V) may include spraying, spin coating, immersion, roll coating, gravure coating and curtain flow coating.

[0034] When applying the compounds (IV) and (V), these compounds are preferably dissolved, suspended or dispersed in a solvent. The solvent is not particularly limited. For example, in the case of the compound (IV), conventionally used organic solvents, such as acetone, methyl isobutyl ketone and ethanol, can be used, while, in the case of the compound (V), useful solvents include perfluorohexane, perfluoro-1,3-dimethylcyclohexane and dichloropentafluoropropane (HCFC-225).

[0035] Although the thickness of the fluorine-containing polymer layer in the stainproof substrate of the present invention is not limited, the thickness is preferably 0.001 μm to 0.03 μm .

[0036] The types of the substrate to be stainproof in the present invention are not particularly limited. Accordingly, examples of the substrate may include glass, resins, metals, ceramics, wood, porcelain, stone and leather.

[0037] As to the glass substrates, the substrates are not particularly limited so long as they are made from glass. Examples of the substrate may include glass for use on the surface of a variety of articles such as show windows, mirrors, water baths, windowpanes, tablewares and glass cases.

[0038] As to the resin substrates, the substrates are not particularly limited and examples thereof include articles made not only from natural resins but also from synthetic resins.

[0039] Examples of the natural resins may include cellulose and japan lacquer. Examples of the synthetic resins may include polyamide resins, polyacrylate resins, polyamideimide resins, polyvinyl acetate resins, polyvinyl chloride resins, phenol resins, urea resins, melamine resins, epoxy resins and polyester resins.

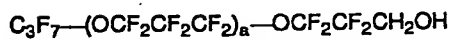
[0040] Examples of the metal substrate may include iron, zinc, lead, copper and aluminum.

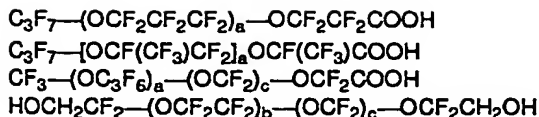
[0041] Meanwhile, the compound (VII) (silane coupling agent and the like), the compound (V) and the compound (VI) are all commercialized and are easily available.

[0042] For example, the following compounds are commercially available as the compound (VII) (silane coupling agent and the like) by Toray Dow Corning Co., Ltd.

Product name	Chemical name	Structural formula	Typical properties		
			Molecular weight	Specific gravity	Refractive index
AX43-062	γ -mercaptopropylmethyltrimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3	180.3	0.99	1.449
AY43-024	hydroxypropyltrimethoxysilane	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3	180.3	0.90	1.365
SH6020	γ -(2-aminoethyl)aminopropyltrimethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	222.1	1.03	1.444
SH6020P	γ -(2-aminoethyl)aminopropyltrimethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3	206.1	0.97	1.449
SZ6023	γ -(2-aminoethyl)aminopropyltrimethoxysilane	$\text{CH}_2=\text{CH}-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3	236.1	1.07	1.427
SH6040	γ -glycidopropyltrimethoxysilane	$\text{CH}_2=\text{CH}-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3	198.5	1.08	1.418
SH6076	γ -chloropropyltrimethoxysilane	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	196.2	1.06	1.442
SH6062	γ -mercaptopropyltrimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	182.7	1.03	1.426
AX43-110	γ -chloropropylmethyltrimethoxysilane	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ CH_3			

[0043] On the other hand, the following compounds are commercially available as the compounds (V) and (VI).





[0044] In addition, $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OCF}_2\text{CF}_2\text{COF}$ is available as one of raw materials for these compounds (JP-B No. Showa 63-43419 (43419/1988)). A compound such as $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OCF}_2\text{CF}_2\text{CN}$ can be derived therefrom (Ind. Eng. Chem. Res., 1987, 26, 1980). Reduction of the foregoing compound provides $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OCF}_2\text{CF}_2\text{CH}_2\text{NH}_2$.

[0045] The reaction between $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OC}_2\text{F}_4\text{CH}_2\text{OH}$ and epichlorohydrin provides

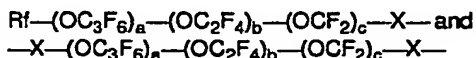


[0046] The reaction between $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OC}_2\text{F}_4\text{CH}_2\text{OH}$ and a metal hydride MH_x (M is a metal and x is a number of 1 to 6) (e.g., KH and NaH) provides $\text{C}_3\text{F}_7-(\text{OC}_3\text{F}_6)_a-\text{OC}_2\text{F}_4\text{CH}_2\text{OM}$ (metal alcoholate).

[0047] A fluorine-containing compound (I) or (II) terminated with a metal coupling group can be obtained by chemically combining the perfluoropolyether (V) or (VI) with the compound (VII) through the reaction between the polar groups thereof.

[0048] Examples of the reaction between the polar groups are given below.

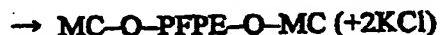
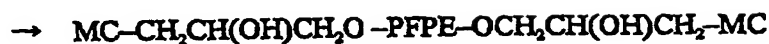
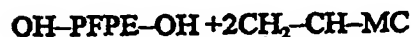
[0049] In the following, for the purpose of simplification,



in the general formulae (V) and (VI) are expressed as "PFPE". Likewise, $\text{Z}-\text{M}-\text{P}_n\text{R}_{m-n}$ in the general formula (IV) is expressed as "MC".

[0050] Accordingly, the general formula (V) is expressed as "PFPE-T", the general formula (VI) as "T-PFPE-T", and the general formula (IV) as "MC-Q". In this case, the general formula (I) is "PFPE-Y-MC" and the general formula (II) is "MC-Y-PFPE-Y-MC".

[0051] If an ordinary polar group is selected as T and Q, the fluorine-containing polymers (I) and (II) can be obtained by, for example, the following reactions.



[0052] Since a metal coupling material is unstable to water, it is preferable that the coating film on the substrate surface is formed by a procedure in which a compound (IV) is first applied to the substrate surface and thereafter the compound (IV) is reacted with a compound (V) or (VI) if water is generated as a by-product.

[0053] The substrates whose surface is rendered stainproof according to the present invention can be used as parts of the following articles which are liable to be stained.

[0054] Home electric appliances such as blades of electric fans, doors of electronic ovens, and surface of electric refrigerators; office articles such as contact glass of copying machines, mirrors of OHP main bodies, OHP sheets, key boards, telephones and desks; home articles such as glass, doors of cupboards, mirrors, windowpanes, lampshades and chandeliers; architectural members such as show windows, telephone boxes and glass of water baths; automotive parts such as glass and paint films on bodies of vehicles; personal ornaments such as frames of a pair of spectacles, glass of underwater cameras, goggles, helmets and cover glass of dial plates of watches; play goods such as glass of pinball tables, trumps and mahjong tiles; and paint film surfaces of articles such as furniture and piano.

[0055] Ornament pieces such as necktie pins, necklaces and pierced earring; metal or plated articles such as faucets of water supply, metal wind instruments, wooden wind instruments, golf clubs, door handles, dumbbells and knives; stone articles such as gravestones, go game stone pieces and marbles; paper products such as wall paper, paper for sliding partitions, books, posters and photographs; and leather products such as wallets, shoes, bags, wrist watch bands and baseball gloves.

PREFERRED EMBODIMENT OF THE INVENTION

[0056] In order to further illustrate the present invention, the following specific examples are given. It should be understood that the following examples do not limit the present invention.

Example 1

[0057] A 500 mL four-neck flask equipped with a stirrer, dropping funnel, refluxing condenser and thermometer was

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charged with a solution prepared by dissolving 180 g (0.5 mol) of $C_3F_7-(OCF_2CF_2CF_2)_a-OCF_2CF_2COF$ (having a number-average molecular weight of 3,600) in 500 mL of dichloropentafluoropropane (HCFC-225) and the atmosphere of the system was sufficiently replaced with nitrogen. Then, under a nitrogen gas stream, 90 g (0.5 mol) of hydroxypropyltrimethoxysilane (AY-43-024 manufactured by Toray Dow Corning Co., Ltd.) was added dropwise from a dropping funnel to the flask.

[0058] Upon completion of the addition, the temperature of the system was raised to 50°C and the reaction was kept for 4 hours. After the reaction, 250 g of a fluorine-containing polymer $[C_3F_7-(OCF_2CF_2CF_2)_a-CF_2CF_2COOCH_2CH_2CH_2Si(OCH_3)_3]$ was obtained by removing the solvent HCFC-225 under a reduced pressure.

[0059] According to the infrared absorption spectrum of the reaction product, the absorption (1890 cm^{-1}) due to $-COF$ of the starting material disappeared completely and new absorption (1780 cm^{-1}) due to $-COO-$ of ester was found.

[0060] The results of the elemental analysis of the fluorine-containing polymer were as follows.

	C	F	O	H	Si
Calculated (%)	22.7	65.2	10.9	0.4	0.8
Found (%)	21.5	65.8	11.3	0.5	0.9

Example 2

[0061] A 500 mL four-neck flask equipped with a stirrer, dropping funnel, refluxing condenser and thermometer was charged with a solution prepared by dissolving 100 g (0.5 mol) of $C_3F_7-(OCF_2CF_2CF_2)_a-OCF_2CF_2CH_2OH$ (having a number-average molecular weight of 2,000) in 500 mL of dichloropentafluoropropane (HCFC-225) and with 1 mL of trifluoroboron ether as a catalyst. The atmosphere of the system was sufficiently replaced with nitrogen. Then, under a nitrogen gas stream, 100 g (0.5 mol) of γ -glycidoxypolytrimethoxysilane (SH6040 manufactured by Toray Dow Corning Co., Ltd.) was added dropwise from a dropping funnel to the flask.

[0062] Upon completion of the addition, the temperature of the system was raised to 50°C and the reaction was kept for 4 hours. After the reaction, 175 g of a fluorine-containing polymer $[C_3F_7-(OCF_2CF_2CF_2)_a-OCF_2CF_2CH_2OCH_2CH(OH)CH_2OCH_2CH_2CH_2Si(OCH_3)_3]$ was obtained by removing the solvent HCFC-225 under a reduced pressure.

[0063] According to the infrared absorption spectrum of the reaction product, the absorption (795 cm^{-1} , 820 cm^{-1}) due to epoxy of the starting material disappeared completely.

[0064] The results of the elemental analysis of the fluorine-containing polymer were as follows.

	C	F	O	H	Si
Calculated (%)	22.4	61.1	12.3	1.0	1.2
Found (%)	23.9	61.4	12.5	0.9	1.3

Example 3

[0065] A 500 mL four-neck flask equipped with a stirrer, dropping funnel, refluxing condenser and thermometer was charged with a solution prepared by dissolving 100 g (0.5 mol) of $HOCH_2CF_2-(OCF_2CF_2)_b-(OCF_2)_c-OCF_2CH_2OH$ (having a number-average molecular weight of 2,000) in 500 mL of m-xylene hexafluoride and with 1 mL of trifluoroboron ether as a catalyst. The atmosphere of the system was sufficiently replaced with nitrogen. Then, under a nitrogen gas stream, 200 g (1 mol) of γ -glycidoxypolytrimethoxysilane (SH6040 manufactured by Toray Dow Corning Co., Ltd.) was added dropwise from the dropping funnel to the flask.

[0066] Upon completion of the addition, the temperature of the system was raised to 50°C and the reaction was kept for 4 hours. After the reaction, 250 g of a fluorine-containing polymer $[(H_3CO)_3SiCH_2CH_2CH_2OCH_2CH(OH)CH_2OCH_2CF_2-(OCF_2CF_2)_b-(OCF_2)_c-OCF_2CH_2OCH_2CH(OH)CH_2OCH_2CH_2CH_2Si(OCH_3)_3]$ was obtained by removing the solvent m-xylene hexafluoride under a reduced pressure.

[0067] According to the infrared absorption spectrum of the reaction product, the absorption (795 cm^{-1} , 820 cm^{-1})

due to epoxy of the starting material disappeared completely.

[0068] The results of the elemental analysis of the fluorine-containing polymer were as follows.

	C	F	O	H	Si
Calculated (%)	26.1	51.9	17.5	1.9	2.6
Found (%)	25.5	51.5	18.4	1.9	2.7

Examples 4 to 5 and Comparative Example 1

[0069] The polymer obtained in Example 1 (Example 4), the polymer obtained in Example 2 (Example 5), and a commercially available, fluorine-containing silane coupling agent, $C_8F_{17}CH_2CH_2Si(OCH_3)_3$, KBM7803 manufactured by Shin-Etsu Chemical Co., Ltd. (hereinafter simply referred to as "commercial product") (Comparative Example 1) were dissolved, respectively, in perfluorohexane to prepare 0.1% by weight solutions. These solutions were used as stainproof treatment liquids.

[0070] Meanwhile, glass plates for use as substrates were washed with water and thereafter well washed with methanol and acetone. The glass plates thus prepared were immersed in the treatment liquid for 10 seconds, taken out of the liquid, and then dried for 60 minutes at room temperature. Then, the glass plates were subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the glass plates were dried in air and subjected to various measurements.

Example 6

[0071] The polymer obtained in Example 3 was dissolved in perfluorohexane to prepare a 0.1% by weight solution. This solution was used as a stainproof treatment liquid.

[0072] Meanwhile, a glass plate for use as a substrate was washed with water and thereafter well washed with methanol and acetone. The glass plate thus prepared was immersed in the treatment liquid for 10 seconds, taken out of the treatment liquid, and then dried for 60 minutes at room temperature. Then, the glass plate was subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the glass plate was dried in air and subjected to various measurements.

Example 7

[0073] γ -(2-aminoethyl)aminopropyltrimethoxysilane (SH6020 manufactured by Toray Dow Corning Co., Ltd.) (silane coupling agent) was dissolved in acetone to prepare a 0.1% by weight solution.

[0074] Meanwhile, a glass plate for use as a substrate was washed with water and thereafter well washed with methanol and acetone. The glass plate thus prepared was immersed in the solution for 1 minute, taken out of the solution, and then dried for 1 hour at room temperature.

[0075] Next, $C_3F_7-(OCF_2CF_2CF_2)_n-OCF_2CF_2COOH$ (having a number-average molecular weight of 5,000) was dissolved in perfluorohexane to prepare a 0.5% by weight solution. In this solution, the glass plate, which had been treated with the silane coupling agent, was immersed for 1 minute. The glass plate was then taken out of the solution and dried for 1 hour at 100°C.

[0076] Then, the glass plate was subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the glass plate was dried in air and subjected to various measurements.

Example 8

[0077] γ -mercaptopropyltrimethoxysilane (SH6062 manufactured by Toray Dow Corning Co., Ltd.) (silane coupling agent) was dissolved in acetone to prepare a 0.1% by weight solution.

[0078] Meanwhile, a glass plate for use as a substrate was washed with water and thereafter well washed with methanol and acetone. The glass plate thus prepared was immersed in the solution for 1 minute, taken out of the solution, and then dried for 1 hour at room temperature.

[0079] Next, $C_3F_7-(OCF_2CF_2CF_2)_n-OCF_2CF_2COOH$ (having a number-average molecular weight of 2,000) was dissolved in perfluorohexane to prepare a 0.5% by weight solution. In this solution, the glass plate, which had been treated with the silane coupling agent, was immersed for 1 minute. The glass plate was then taken out of the solution

and dried for 1 hour at 100°C.

[0080] Then, the glass plate was subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the glass plate was dried in air and subjected to various measurements.

[0081] The properties of the glass plates treated were evaluated according to the following methods.

(1) As to the adhesion of fingerprints, the glass plate samples were stained with fingerprints and the ease of the fingerprints adherence were visually inspected.

○ : the amount of adhered fingerprint is slight so that the adhered fingerprint is not apparent.

X: the amount of fingerprint is the same as that on an untreated glass plate.

Δ: difficult to give a clear rating between the two described above

(2) As to the ease in fingerprint removal, the surfaces of the samples used in the evaluation of the adhesion of fingerprints were wiped by one cycle of reciprocating movement of KIM Wipe (manufactured by Jujo Kimberley Co., Ltd.) and the ease in removal of the fingerprints was visually inspected.

○ : fingerprints can be completely removed.

Δ: fingerprint wiping marks remains.

X: fingerprints wiping marks extend and removal of the marks is difficult.

(3) Contact angle with water was measured using a contact angle meter (model CA-DT manufactured by Kyowa Kaimem Kagaku Kikai Co., Ltd.).

[0082] The results are given below.

	Adhesion of fingerprints	Ease in fingerprint removal	Contact angel with water
Example 4	○	○	114°
Example 5	○	○	110°
Example 6	○	○	109°
Example 7	○	○	115°
Example 8	○	○	109°
Comparative Example 1	Δ	X	109°

Example 9 and Comparative Example 2

[0083] The polymer obtained in Example 1 (Example 9) and a commercially available product (Comparative Example 2) were dissolved, respectively, in perfluorohexane to prepare 0.1% by weight solutions.

[0084] Meanwhile, aluminum plates for use as substrates (each having a thickness of 0.5 mm and in compliance with JIS H 4000 (A1050P)) were washed with water and thereafter well washed with methanol and acetone.

[0085] The aluminum plates thus prepared were immersed in the solutions for 10 seconds, taken out of the solution, and then dried for 60 minutes at room temperature. Then, the aluminum plates were subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the aluminum plates were dried in air and subjected to various measurements.

Comparative Example 3

[0086] The aluminum plate in Example 9 was used without being treated.

Example 10

[0087] γ -(2-aminoethyl)aminopropyltrimethoxysilane (SH6020 manufactured by Toray Dow Corning Co., Ltd.) (silane

coupling agent) was dissolved in acetone to prepare a 0.1% by weight solution.

[0088] Meanwhile, an aluminum plate for use as a substrate (having a thickness of 0.5 mm and in compliance with JIS H 4000 (A1050P)) was washed with water and thereafter well washed with methanol and acetone.

[0089] The aluminum plate thus prepared was immersed in the solution for 1 minute, taken out of the solution, and then dried for 60 minutes at room temperature.

[0090] Next, $C_3F_7-(OCF_2CF_2CF_2)_a-OCF_2CF_2COOH$ (having a number-average molecular weight of 5,000) was dissolved in perfluorohexane to prepare a 0.5% by weight solution. In this solution, the aluminum plate, which had been treated with the silane coupling agent, was immersed for 1 minute. The aluminum plate was then taken out of the solution and dried for 1 hour at 100°C.

[0091] Then, the aluminum plate was subjected to ultrasonic cleaning in perfluorohexane for 5 minutes to remove excessive stainproof treatment components. Then, the aluminum plate was dried in air and subjected to the following durability test.

[0092] The durability test was conducted in the following manner. The same sample surface was wiped by 100 cycles of reciprocating movement of KIM Wipe (manufactured by Jujo Kimberley Co., Ltd.) under a load of 900 g by using an electric clock meter (416-TM1 model manufactured by Yasuda Seiki Seisakusho Co., Ltd.). The contact angles with water before and after the wiping operations were measured. The contact angle with water was measured using a contact angle meter (model CA-DT manufactured by Kyowa Kaimem Kagaku Kikai Co., Ltd.).

[0093] The results are given below.

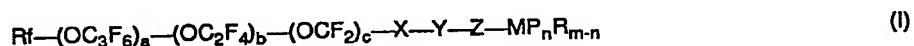
	Contact angle with water before wiping operation	Contact angle with water after wiping operation
Example 9	112°	107°
Example 10	115°	111°
Comparative Example 2	111°	98°
Comparative Example 3	88°	—

EFFECTS OF THE INVENTION

[0094] When used as a stainproof coating layer, the fluorine-containing polymer of the present invention provides a stainproof substrate having an excellent stainproof property against particularly fingerprints. Accordingly, the fluorine-containing polymer of the present invention can be suited for use in a variety of substrates such as glass, resins, metals, ceramics, wood, porcelain, stone and leather.

Claims

1. A fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (I):



wherein Rf is a perfluoroalkyl group;

a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1;

X is a group represented by the formula: $-(O)_d-(CF_2)_e-(CH_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula);

Y is a divalent polar group;

Z is a group represented by the formula: $-(CH_2)_g-$ (where g is 0 or a number equal to or greater than 1);

M is a metal atom;

R is a hydrocarbon group;

P is a hydrolyzable polar group;

m is an integer equal to "(valency of M) - 1";

n is an integer of 1 to m;

with the proviso that the presence order of the bracketed repeating units is arbitrary in the formula; $-\text{OC}_3\text{F}_6-$ represents either $-\text{OCF}_2\text{CF}_2\text{CF}_2-$ or $-\text{OCF}(\text{CF}_3)\text{CF}_2-$; and $-\text{OC}_2\text{F}_4-$ represents either $-\text{OCF}_2\text{CF}_2-$ or $-\text{OCF}(\text{CF}_3)-$.

2. A fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (II):



wherein a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1;

X is a group represented by the formula: $-(\text{O})_d-(\text{CF}_2)_e-(\text{CH}_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula;

Y is a divalent polar group;

Z is a group represented by the formula: $-(\text{CH}_2)_g-$ (where g is 0 or a number equal to or greater than 1);

M is a metal atom;

R is a hydrocarbon group;

P is a hydrolyzable polar group;

m is an integer equal to "(valency of M) - 1";

n is an integer of 1 to m;

with the proviso that the presence order of the bracketed repeating units is arbitrary in the formula; $-\text{OC}_3\text{F}_6-$ represents either $-\text{OCF}_2\text{CF}_2\text{CF}_2-$ or $-\text{OCF}(\text{CF}_3)\text{CF}_2-$; and $-\text{OC}_2\text{F}_4-$ represents either $-\text{OCF}_2\text{CF}_2-$ or $-\text{OCF}(\text{CF}_3)-$.

3. A fluorine-containing polymer having a number-average molecular weight of 500 to 100,000 and represented by the following general formula (III):



wherein Rf is a perfluoroalkyl group;

a is a number equal to or greater than 1;

X is a group represented by the formula: $-(\text{O})_d-(\text{CF}_2)_e-(\text{CH}_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula);

Y is a divalent polar group;

Z is a group represented by the formula: $-(\text{CH}_2)_g-$ (where g is 0 or a number equal to or greater than 1);

R is a hydrocarbon group;

P is a hydrolyzable polar group; and

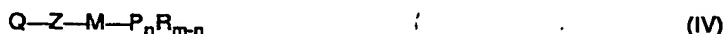
n is an integer of 1 to 3.

4. A stainproof substrate comprising a substrate, and a layer which is provided on said substrate and composed of the fluorine-containing polymer of Claim 1.

5. A stainproof substrate comprising a substrate and a layer which is provided on said substrate and composed of the fluorine-containing polymer of Claim 2.

6. A stainproof substrate comprising a substrate and a layer which is provided on said substrate and composed of the fluorine-containing polymer of Claim 3.

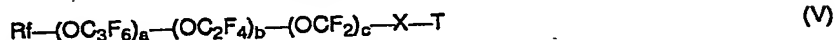
7. A process for preparing the stainproof substrate of Claim 4 comprising the steps of forming on a surface of the substrate a layer of a compound represented by the following general formula (IV):



wherein Z is a group represented by the formula : $-(CH_2)_g-$ (where g is 0 or a number equal to or greater than 1);

M is a metal atom;
 R is a hydrocarbon group;
 P is a hydrolyzable polar group;
 m is an integer equal to "valency of M" - 1";
 n is an integer of 1 to m; and
 Q is a polar group;

and thereafter reacting said layer with a compound represented by the following general formula (V):



wherein Rf is a perfluoroalkyl group;

a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1;

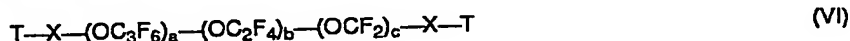
X is a group represented by the formula : $-(O)_d-(CF_2)_e-(CH_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula); and

T is a polar group;
 with the proviso that the presence order of the bracketed repeating units is arbitrary in the formula; $-OC_3F_6-$ represents either $-OCF_2CF_2CF_2-$ or $-OCF(CF_3)CF_2-$; and $-OC_2F_4-$ represents either $-OCF_2CF_2-$ or $-OCF(CF_3)-$.

8. A process for preparing the stainproof substrate of Claim 5 comprising the steps of forming on the surface of the substrate a layer of a compound represented by the following general formula (IV):



wherein Q, Z, M, P, R, m and n are the same as defined in the formula (IV) of Claim 7, and thereafter reacting said layer with a compound represented by the following general formula (VI):



wherein Rf is a perfluoroalkyl group;

a, b and c independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of a, b and c is at least 1;

X is a group represented by the formula : $-(O)_d-(CF_2)_e-(CH_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula); and

T is a polar group;
 with the proviso that the presence order of the bracketed repeating units is arbitrary in the formula; $-OC_3F_6-$ represents either $-OCF_2CF_2CF_2-$ or $-OCF(CF_3)CF_2-$; and $-OC_2F_4-$ represents either $-OCF_2CF_2-$ or $-OCF(CF_3)-$.

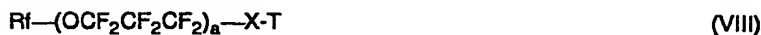
9. A process for preparing the stainproof substrate of Claim 6 comprising the steps of forming on the surface of the substrate a layer of a compound represented by the following general formula (VII):



wherein Z is a group represented by the formula : $-(CH_2)_g-$ (where g is 0 or a number equal to or greater than 1);

R is a hydrocarbon group;
 P is a hydrolyzable polar group;
 n is an integer of 1 to 3; and
 Q is a polar group, and thereafter reacting said layer with a compound represented by the following general

formula (VIII):



wherein Rf is a perfluoroalkyl group;

a is a number equal to or greater than 1;

X is a group represented by the formula: $-(\text{O})_d-(\text{CF}_2)_e-(\text{CH}_2)_f-$ (where d, e and f independently represent 0 or a number equal to or greater than 1, with the proviso that the sum of e and f is at least 1, and the presence order of the bracketed repeating units is arbitrary in the formula); and

T is a polar group.

10. A process for preparing the fluorine-containing polymer of Claim 1 comprising the steps of carrying out a reaction between a compound represented by the general formula (IV):



wherein Q, Z, M, P, R, m and n are the same as defined in the formula (IV) of Claim 7, and a compound represented by the following general formula (V):

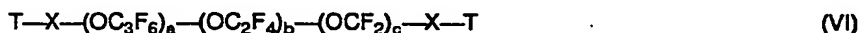


wherein Rf, T, X, a, b and c are the same as defined in the formula (V) of Claim 7.

11. A process for preparing the fluorine-containing polymer of Claim 2 comprising the steps of carrying out a reaction between a compound represented by the general formula (IV):

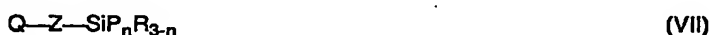


wherein Q, Z, M, P, R, m and n are the same as defined in the formula (IV) of Claim 7, and a compound represented by the following general formula (VI):

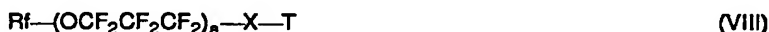


wherein T, X, a, b and c are the same as defined in the formula (VI) of Claim 8.

12. A process for preparing the fluorine-containing polymer of Claim 3 comprising the steps of carrying out a reaction between a compound represented by the general formula (VII):



wherein Q, Z, P, R and n are the same as defined in the formula (VII) of Claim 9, and a compound represented by the following general formula (VIII):



wherein T, Rf, X and a are the same as defined in the formula (VIII) of Claim 9.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/JP98/01948

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ C08G65/32, C09D171/02 // C08G77/46, C09D183/12 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ C08G65/00-65/48, C09D171/00-171/14 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI/L (QUESTEL)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 5-117283, A (Mitsubishi Rayon Co., Ltd.), May 14, 1993 (14. 05. 93), Claims ; Par. No. [0013] (Family: none)	1, 3, 4, 6, 7, 9 2, 5, 8
X	JP, 5-279499, A (Asahi Glass Co., Ltd.), October 26, 1993 (26. 10. 93), Claims ; Par. Nos. [0018] to [0020], [0026] to [0030], [0039], [0050] & EP, 513690, A2 & US, 5314731, A	1, 3 2, 4-9
PX PY PA	JP, 9-137027, A (Shin-Etsu Chemical Co., Ltd.), May 27, 1997 (27. 05. 97), Claims ; Par. Nos. [0006], [0043], [0044] & US, 5705591, A	2 5, 8 1, 3, 4, 6, 7, 9
X A	JP, 62-48724, A (Minnesota Mining and Manufacturing Co.), March 3, 1987 (03. 03. 87), Claims & US, 3810874, A	2 1, 3-9
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search July 21, 1998 (21. 07. 98)		Date of mailing of the international search report August 4, 1998 (04. 08. 98)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

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EP 0 978 524 A1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/01948

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 6-256500, A (Shin-Etsu Chemical Co., Ltd.), September 13, 1994 (13. 09. 94), Claims (Family: none)	1-9
A	JP, 7-505399, A (E.I. Du Pont de Nemours & Co.), June 15, 1995 (15. 06. 95), Claims & WO, 9320084, A1 & EP, 629205, A1	1-9

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